

**10/566046**

WO2005/014934

PCT/EP2004/051701

**IAP20 Rec'd PCT/PTR 26 JAN 2006**

**Method for loading a fibrous stock suspension  
and arrangement to accomplish said method.**

The invention relates to loading of a fibrous stock suspension with calcium carbonate.

Several methods for loading chemical pulp fibers with calcium carbonate are already known. A method is described in US 6,413,365 B1 where the fibrous material is transported via a supply line together with calcium oxide and/or calcium hydroxide which are contained in said suspension. From there, the fibrous stock suspension is transported into a rotating distribution device. A reaction gas is fed in a ring shaped pattern into the fibrous stock suspension; this causes formation of calcium carbonate crystals in the fibrous suspension. The calcium carbonate crystals are distributed in the fibrous stock suspension through the rotating distributor device. This process is known as Fiber Loading Process.

Additional methods and arrangements for loading fibers in a fibrous stock suspension with a filler or additives are known from DE 101 07 448 A1 and DE 101 13 998 A1.

With the assistance of these known processes, cigarette paper, cardboard and all types of packaging papers, all types of kraft sack paper and papers containing fillers can be produced. The following applies to the production of cigarette paper: cigarette paper has a base weight of 16 to 26 g/m<sup>2</sup>. It is frequently enhanced with an impressed water mark and should be very thin, capable of glowing combustion, and tasteless. It should also possess good optical values with regard to the brightness. The capability of glowing combustion is usually achieved by impregnation in order to leave an attractive white ash.

Cigarette paper is normally produced from linen or hemp fibers, cotton, sulfate pulp, paper machine broke, as well as from other fiber sources. The filler content in cigarette paper is between 5 and 40%, whereby 30% is considered as a standard value.

Packaging papers and cardboards can be divided into three categories: Container board for packaging purposes, container board for applications in the field of consumer packaging and specialized papers such as wall paper, book spines, etc. Packaging papers are normally produced as multi-ply products having basis weights higher than 150 g/m<sup>2</sup>. The freeness varies from 600 to 50 CSF or 20 to 80 °SR, relative to the produced end product.

Kraft sack papers require a high porosity and a high mechanical strength in order to meet the high demands that occur due to the rough handling during the filling process and the duration of their use, as is the case for example with cement bags. The paper must be strong enough to absorb impacts and must have an accordingly high energy absorption capacity. The sack paper must also be porous and sufficiently air permeable in order to facilitate effortless filling. Sack papers are produced, for example from a long fibered kraft pulp into product having a basis weight of between 70 and 80 g/m<sup>2</sup>, and having a freeness of between 600 to 425 CSF or 20 to 30 °SR. In addition a medium freeness as described above is strived for. This is usually achieved through high consistency refining whereas in the case of conventional paper grades, for example graphic papers, low consistency refining is utilized. The result of the high consistency refining is good adhesion of the fibers to each other as well as a high porosity. The sack paper is predominantly produced from bleached and unbleached fibers, whereby a filler content of 5 to 15% may be present in the produced sack paper.

Filter paper requires a high controlled porosity and pore distribution. It must have a sufficiently high mechanical strength to counteract the flow of the medium that is to be filtered.

Filter paper is produced, having a basis weight of 12 to 1200 g/m<sup>2</sup>. For example, an air filter would have a basis weight of between 100 and 200 g/m<sup>2</sup>, an oil and fuel filter between 50 and 80 g/m<sup>2</sup>, a food stuff filter to 1000 g/m<sup>2</sup>, a coffee filter to 100 g/m<sup>2</sup>, a tea bag between 12 and 20 g/m<sup>2</sup> and a vacuum bag between 100 and 150 g/m<sup>2</sup>. All filters are produced from a multitude of fibers, such as chemical pulp fibers, bleached and unbleached fibers, kraft pulp, DIP (deinked) paper, recycled fibers, TMP (thermo mechanical) paper, etc.

It is the objective of the current invention to further improve a method of the type referred to at the beginning.

In accordance with the current invention this objective is met by a method comprising the following process steps:

- Feeding of calcium hydroxide in liquid or dry form, or of calcium oxide into the fibrous stock suspension,
- Feeding of gaseous carbon dioxides into the fibrous stock suspension,
- Precipitation of calcium carbonate through the carbon dioxide and
- Refining of the fibrous stock suspension during the loading process.

The current invention describes a method for the production of fiber loaded precipitated calcium carbonate (FLPCC) and to simultaneously undergo a refining process, whereby the fiber raw material that is to be loaded may consist of recycling paper, DIP (deinked paper), secondary fibers, bleached or unbleached pulp, mechanical pulp, bleached or

unbleached sulfate pulp, broke, linen, cotton, and/or hemp fibers (predominantly cigarette paper) and/or any paper raw material that can be utilized on a paper machine, irrespective of whether or not the end product contains a filler that was produced by a precipitation process in batch reactors or by a refining process, or whether talcum, titanium dioxide ( $TiO_2$ ), silicon, etc. are used. The refining process is also referred to as GCC process (GCC = ground calcium carbonate).

When a fibrous stock suspension is processed with a fiber loading technology a completely new product for application in paper production results, with new and improved characteristics compared to a product according to the current state of the art. The fiber loading technology permits precipitation of a filler - especially calcium carbonate - that is uniformly distributed and adhered to, in and between the paper fibers directly in the stock preparation of a paper mill. It also allows the treated fibrous stock to undergo a fiber treatment in a refiner simultaneously with the precipitation process.

The process for the production of precipitated calcium carbonate with simultaneous refining with the assistance of the fiber loading combination process occurs according to the process data which is described in further detail below. In this context please also refer to DE 101 07 448 A1, DE 101 13 998 A1 and US 6 413 365 B1.

In accordance with the FLPCC combination process described under this invention the filler material utilized according to the current state of the art is replaced with the filler material produced according to the fiber loading combination process technology. The range of application of the filler produced with the fiber loading combination process technology extends to applications within the paper production of all paper grades, including cigarette papers, filter papers, kraft sack paper grades and cardboard and packaging papers that have a filler content of between 1 and 60% and /or a white liner

having a filler content of between 1 and 60%. The loaded and produced paper grades can be produced on a paper machine from a recycling paper, deinked paper (DIP), secondary fibers, bleached or unbleached pulp, mechanical pulp, bleached or unbleached sulfate pulp, broke, linen, cotton, and/or hemp fibers (predominantly for cigarette paper) and/or any paper raw material, irrespective of whether or not the end product contains a filler.

Fibrous stock produced with the fiber loading combination process technology generally possesses a superior dewatering characteristic than a fibrous stock produced according to another method; the improvement in the dewatering capacity is between 5 to 100 ml CSF or 0.2 to 15° SR, depending upon the required freeness. The stock or pulp produced according to the fiber loading process further possesses a low water retention value of 2 to 25%, depending upon the raw material that is used in production. This permits a more effective production of various paper grades, for example FL (FL = fiber loaded) copy and printing paper of all types, FL coating paper of all types, FL news print of all types and FL cigarette paper of all types, FL B&P paper of all types, FL kraft sack paper of all types and FL filter paper, since the water in the stock suspension can be removed faster. The stock therefore dries accordingly faster.

In the instance of FL cigarette paper, FL B&P paper, FL kraft sack paper and FL filter paper which do not require fillers, the exposed filler can be removed by means of an additionally provided washing process prior to the refining process, following the refining process or after running through the headbox vat or prior to feeding into the paper machine. This applies to the filler that is not deposited in or on the fibers and can be washed out accordingly. The fibers themselves are still contain filler, inside and out so that the positive effects of the fiber loading technology can be taken advantage of.

The fiber loading technology may be utilized prior to or after the refining process, depending on what requirements are put upon the end product.

Compared to the current state of the art, a higher freeness value can be achieved with the fiber loading combination technology, since up to 50% of refining energy can be saved; this has an especially positive influence with all the paper grades which pass through a refining process during their production, or which possess a very high freeness value, for example FL-cigarette papers, FL B&P papers, FL kraft sack papers and FL filter papers. In particular, these are FL cigarette papers having 100 to 25 CSF or 68 to 90° SR, FL B&P papers having 600 to 50 CSF or 20 to 80° SR, FL sack papers having 600 to 425 CSF or 20 to 30° SR and FL filter papers having 600 to 350 CSF or 20 to 35° SR.

The high mechanical strengths in the end product which are achieved through the high freeness value positively affect the production of FL cigarette papers, FL B&P papers, FL sack papers and FL filter papers since, due to process based mechanical loads in the various section of the paper machine, such as the press section, the dryer section and in the area where the web is wound, the produced intermediate product and the end product which is to be produced bears a high mechanical load due to utilization of winders, rewinders and converting machinery. Great mechanical stresses occur on the paper, especially in the production of cigarette paper, which are also partially attributed to the low basis weight and the utilization of winders.

More effective drying to a residual moisture content of 1 to 20% permits an increase in efficiency for all paper grades. A higher water retention capacity, i.e. 1 to 25% results in a positive influence upon remoistening which is lower in the manufacturing process, as well as upon the printability of the produced web. An additional advantage for all paper grades is the greater brightness or the higher optical values with around 15 or more lightness points, which is to be emphasized in the production of all grades of paper and cardboard, with or without white liner. By using the fiber loading technology the optical values – for example in cigarette papers – are also improved by up to 10 lightness points.

An additional advantage of fiber loading with the above referenced paper grades is found in that for special applications calendering is provided and in doing so the so-called blackening due to deposits of FL particles in, around and on the fibers is suppressed or eliminated through utilization of the fiber loading process.

Advantageous design forms of the current invention can be seen in the sub-claims, the description and the drawing.

In accordance with one design form of the current invention aqueous fibrous stock material, especially aqueous paper stock having a consistency of 0.1 to 20%, preferably between 2 and 15% is used as primary raw material

In accordance with the current invention calcium hydroxide is mixed as the preferred filler into the aqueous fiber stock material, especially into the paper fiber stock, whereby this has a solids content of between 0.01 and 60%. In accordance with the current invention utilization of a source material other than calcium hydroxide or calcium oxide for formation of the filler is also feasible.

The calcium hydroxide is added through a static mixer or an intermediate vat. The carbon dioxide is preferably added into a moist fibrous stock suspension having a consistency of 0.1 to 15%, according to the reaction parameters. Calcium carbonate is precipitated in a carbon dioxide gaseous atmosphere.

In accordance with the current invention the refining process is carried out simultaneously with the fiber loading process in an apparatus – the crystallizer; a refining energy in the range between 0.1 and 300 kWh/ton dry paper pulp is applied; a short reaction time of the calcium hydroxide and the carbon dioxide is important in this

context. The energy supply or heat volume, or heating of the paper suspension for the production of crystals in various forms is important for the invention.

Depending upon application of the respective reaction machine, aqueous paper stock with a paper content of between 0.01 and 60% is used as primary raw material.

An advantageous embodiment of the method provides that a refiner, a disperger and/or a fluffer FLPCC reactor are utilized as a reactor and/or a static mixer, whereby the fibrous stock content, especially the paper content is between 0.01 and 15% in the instance of a static mixer; at between 2 and 40% in the instance of a refiner and a disperger and between 15 and 60% in the instance of a fluffer-FLPCC-reactor.

The current invention provides that the dilution water is supplied prior to, during or after the addition of carbon dioxide or calcium hydroxide or calcium oxide. Calcium carbonate precipitates when adding carbon dioxide into a calcium hydroxide solution or suspension. Conversely, the precipitative reaction also occurs, when calcium hydroxide is added to water under a carbon dioxide atmosphere. Diluting water may be added prior to, during or after the addition of carbon dioxide or calcium hydroxide.

An expenditure of energy of between 0.3 and 8 kWh/t, especially between 0.5 and 4 kWh/t is preferably used for the precipitation reaction.

Likewise it can be provided that the process temperature is between -15 °C and 120 °C, especially between 20 and 90 °C.

According to the current invention rhombohedral, scalenohedron and spherical crystals can be formed.

Advantageously, the crystals measure between 0.05 and 5 µm, especially between 0.3 and 2.5 µm. Static and/or moving, especially rotating mixing elements may be utilized. The process is preferably carried out in a pressure range of between 0 and 15 bar, especially between 0 and 6 bar. The pH value is preferably between 6 and 10, especially between 6.5 and 9.5. The reaction time is advantageously between 0.01 minutes and 1 minute, especially between 0.05 seconds and 10 seconds.

The current invention is described in further detail below, citing a design example and with the assistance of the only drawing. This illustrates a schematic view of an apparatus for loading of a fibrous stock suspension.

For the purpose of loading a fibrous stock suspension with calcium carbonate said suspension is transported in a device 1 (Figure) in a pipe line system that is equipped with control valves 10, 12. The control valve 10 is located in a line 14 through which the piping system is connected with a static mixer 16. Diluting water can be fed to said mixer via a valve 18. Also, the addition of a suspension of calcium hydroxide is controlled via an additional valve 22 that is installed in a line 20. This is supplied by a preparation apparatus 24, where solid calcium oxide or calcium hydroxide is fed into water. For this purpose water is supplied to the preparation apparatus 24 via a line that is equipped with a valve 26. The suspension produced in the preparation apparatus is passed into the line 20 via a pump 28.

The diluted fibrous stock suspension to which calcium hydroxide was added flows from the mixer 16 into a line 30 that is equipped with a valve 32. From the line 32 the suspension is immediately fed into a disperger 42 (crystallizer). For the purpose of supplying carbon dioxide, this is connected with a carbon dioxide tank 52 through a line 50 which is equipped with valves 44, 46 and a pump 48. Carbon dioxide is fed from the carbon dioxide tank 52 into the disperger 42 in order to produce the desired precipitation

reaction of calcium hydroxide and carbon dioxide for the formation of calcium carbonate as a filler in the fibers of the fibrous stock. Instead of utilizing a mixer 16, the calcium hydroxide may also be added in from a header tank.

Line 50 is connected via an additional valve 58 with a static mixer 60 whose purpose it is to add additional carbon dioxide to the fibrous stock suspension flowing from the disperger 42 through a line 64 which is equipped with a valve 62.

Fibrous stock suspension that is not treated with calcium hydroxide can additionally be fed into the blend chest 68 via the valve 12 and a line 70.

The fibrous stock suspension flows from the mixer 60 into a blend chest 66 which is equipped with a rotor 68 for the purpose of thoroughly mixing the fibrous stock suspension. From the blend chest 66 the fibrous stock suspension flows either immediately to a headbox in a paper machine, or it is subjected to additional mechanical processing, for example in a refiner feed chest.

In addition, a refiner 80 can be installed in the piping system for the purpose of improving the fibrous stock suspension through an additional refining process. Said refiner is supplied with fibrous stock suspension via a line 82 that branches off line 30. From the refiner 80 the repeatedly refined fibrous stock suspension is brought through a line 84 into line 64 and from there, as described above, into the blend chest 66.

Provisions can additionally be made that carbon dioxide from the carbon dioxide storage tank 52 is supplied to the refiner 80 through a line 86 that branches off line 50 and a static mixer 88 that connects line 86 with line 82.

The inventive design for loading of a fibrous stock suspension with calcium carbonate has the advantage when compared with devices according to the current state of the art that machinery for homogenizing of the fibrous stock suspension, such as a screw press, and a conditioning machine for homogenizing of the fibrous suspension (equalizing reactor) is not required. The ~~container/vessel 82~~ additionally takes over the refining process, providing a considerably simpler arrangement of stock preparation compared to the current state of the art. This refining process serves at the same time as agitation process, in order to deposit the calcium carbonate in the fibers through a shear process.

In the inventive method for preparation of the fibrous stock suspension by means of the fiber loading process, calcium hydroxide (lime hydrate, lime milk) is used which has a solubility in water at 20 °C of 1.65 g/l to 0.7 g/l at 100 °C. A pH value of up to 12.6 is achieved, depending upon how closely the concentration of the solution reaches the maximum value. In commercially available lime hydrate concentrations solids contents of 0 to 60% can be realized, whereby the suspension has a pH-value of 12.6 maximum. The actual volume of lime hydrate in the suspension therefore is comprised of the dissolved component as well as the solids concentration.

For a suspension containing 20% calcium hydroxide in one liter f 20 °C therefore, a dissolved mass of 1.65 g calcium hydroxide and a solids content of 198.35 g result. Since in the fiber loading process the conversion or reaction speed influences the end product of the FL process every effort is made to use the lime hydrate for an as short as possible conversion time.

This is achieved in that for the production of the lime hydrate calcium oxide (Ca) in a medium particle size range of 0.01 to 100 mm, especially in a size range of 0.05 to 50 mm is produced a slaking process.

Component identification list

- |    |                             |
|----|-----------------------------|
| 1  | Apparatus                   |
| 10 | Control valve               |
| 12 | Control valve               |
| 14 | Line                        |
| 16 | Mixer                       |
| 18 | Valve                       |
| 20 | Line                        |
| 22 | Valve                       |
| 24 | Preparation apparatus       |
| 26 | Valve                       |
| 28 | Pump                        |
| 30 | Line                        |
| 32 | Valve                       |
| 42 | Disperger                   |
| 44 | Valve                       |
| 46 | Valve                       |
| 48 | Pump                        |
| 50 | Line                        |
| 52 | Carbon dioxide storage tank |
| 58 | Valve                       |
| 60 | Mixer                       |
| 62 | Valve                       |
| 64 | Line                        |
| 66 | Blend chest                 |
| 68 | Rotor                       |
| 80 | Refiner                     |
| 82 | Line                        |
| 84 | Line                        |
| 86 | Line                        |
| 88 | Mixer                       |